Addressing Geographic Variability in the Comparative Toxicity Potential of Copper and Nickel in Soils

Mikołaj Owsianiak*[,1], Ralph K. Rosenbaum[1], Mark A.J. Huijbregts[2], Michael Z. Hauschild[1]

[1] Division for Quantitative Sustainability Assessment, Department of Management Engineering, Technical University of Denmark, Nils Koppels Alle, Building 426D, DK-2800 Kgs. Lyngby, Denmark

[2] Department of Environmental Science, Institute for Wetland and Water Research, Faculty of Science, Radboud University Nijmegen, P.O. Box 9010, NL-6500 GL Nijmegen, The Netherlands

* corresponding author
e-mail: miow@dtu.dk
tel.: 0045 4525 4805

TOC

Abstract

Comparative toxicity potentials (CTP), in life cycle impact assessment also known as characterization factors (CF), of copper (Cu) and nickel (Ni) were calculated for a global set of 760 soils. An accessibility factor (ACF) that takes into account the role of the reactive, solid-phase metal pool in the soil was introduced into the definition of CTP. Geographic differences in fate, accessibility, bioavailability, and terrestrial toxicity were assessed by combining the USEtox characterization model, empirical regression models, and terrestrial biotic ligand models. The median CTPs for Cu and Ni with 95% geographic variability intervals are 1.4×10^3 ($1.7\times10^2 - 2.0\times10^4$) and 1.7×10^3 ($2.1\times10^2 - 1.1\times10^4$) $m^3/kg\cdot day$, respectively. The geographic variability of 3.5 orders of magnitude in the CTP of Cu is mainly associated with the variability in soil organic carbon and pH. They largely influence the fate and bioavailability of Cu in soils. In contrast, the geographic variability of 3 orders of magnitude in the CTP of Ni can mainly be explained by differences in pore water concentration of magnesium (Mg^{2+}). Mg^{2+} competes with Ni^{2+} for binding to biotic ligands, influencing the toxicity. Our findings stress the

importance of dealing with geographic variability in the calculation of CTPs for terrestrial ecotoxicity of metals.

1. Introduction

Current chemical hazard ranking and scoring schemes, including life cycle impact assessment (LCIA), ignore the fact that metals can exist in many forms with different behavior and toxicity in terrestrial environments, depending on the ambient conditions. Efforts have recently been undertaken to improve the situation. Following the "Clearwater Consensus" on assessing metal hazard in freshwater,[1] Gandhi et al.[2] developed a method for calculating comparative toxicity potentials (CTPs) of metals in aquatic systems taking metal speciation into account in environmental fate, bioavailability and effects. The CTPs (in LCIA also known as characterization factors, CF) ranged over three orders of magnitude. The biggest contributor to the variability in CTPs was the difference in bioavailability, controlled mainly by pH-dependent dissolution and complexation with dissolved organic matter. These findings highlight the need for taking into account environmental chemistry parameters in ecotoxicity assessment of metals.

For soils, metal distribution between the solid phase and solution phase, and speciation in soil pore water control the availability of toxic forms of metals, while protons and base cations can mitigate their ecotoxicity.[3-4] Several aspects should be considered when including speciation in calculating soil-specific CTPs of metals. First, residence time of metals may be high due to sorption of metal to soil constituents such as clay or organic carbon.[5] Second, a significant fraction of the solid-phase metal is not available for partitioning to the solution phase due to differences in reactivity of solid metal forms.[6] Third, geographic variability of environmental chemistry parameters in soil can be high. For example, in soils a variation of six units in pH is not uncommon.[7] Due to the effects of pH and other parameters on metal sorption, speciation and ecotoxicity, it can be expected that CTPs of metals in soil will also be controlled by environmental chemistry and will vary depending on soil type, but the magnitude of this variation and controlling factors are unknown.

The aim of our study was to calculate CTPs for copper (Cu) and nickel (Ni) in terrestrial systems taking into account spatial differences in speciation and toxicity as influenced by the soil chemistry. CTPs were calculated for a set of 760 noncalcareous soils from around the world spanning a wide range of properties. USEtox was employed as a fate model to calculate fate factors (FF) of metals in soil after a unit emission to air.[8-9] This emission route was chosen because emissions to air are a major anthropogenic source of metals in soils.[10] Empirical regression models were used to account for differences in metal partitioning in calculation of the distribution coefficient (K_d) and bioavailability factors (BF), while terrestrial biotic ligand models (TBLM) were chosen as ecotoxicity models to calculate effect factors (EF). Recognizing that the largest metal pool in soil is associated with the solid phase and that only a fraction of this metal pool is reactive,[6] a new factor called accessibility factor (ACF) is introduced into the definition of CTP. Geographic variability in CTP is demonstrated for Cu and Ni, which were chosen due to the availability of TBLMs for several terrestrial species for these two metals.

2. Methods

2.1 Framework

Current Framework for Freshwater Ecotoxicity. The method for calculating CTP of cationic metals in freshwater proposed by Gandhi et al.[2] was taken as a starting point (eq 1). In their method, the CTP is defined as:

$$CTP_{i,s} = FF_{i,s} \cdot BF_s \cdot EF_s \tag{1}$$

where $CTP_{i,s}$ ($m^3/kg_{total\ emitted} \cdot day$) is the comparative toxicity potential of total metal s emitted to compartment i; $FF_{i,s}$ (day) is the fate factor calculated for total metal s in freshwater; BF_s ($kg_{bioavailable}/kg_{total}$) is the bioavailability factor defined as the bioavailable fraction of metal s in freshwater; and EF_s ($m^3/kg_{bioavailable}$) indicates the average toxic potency of the bioavailable fraction of metal s expressed as a Potentially Affected Fraction (PAF) of organisms. The bioavailable fraction in the method of Gandhi et al. refers to the "truly" dissolved metal, including free ions and inorganic complexes.

Proposed Framework for Terrestrial Ecotoxicity. The method of Gandhi et al.[2] is further developed to make it suitable to soils. This is done by introducing the accessibility factor (ACF) into the definition of CTP and modifying the definition of the bioavailability factor (BF) (eq 2):

$$CTP_{i,s} = FF_{i,s} \cdot ACF_s \cdot BF_s \cdot EF_s \tag{2}$$

where $CTP_{i,s}$ ($m^3/kg_{total\ emitted} \cdot day$) is the comparative toxicity potential of total metal s emitted to compartment i; $FF_{i,s}$ (day) is the fate factor calculated for total metal s in soil; ACF_s ($kg_{reactive}/kg_{total}$) is the accessibility factor defined as the reactive fraction of total metal s in soil; BF_s ($kg_{free}/kg_{reactive}$) is the bioavailability factor defined as the free ion fraction of the reactive metal s in soil, and EF_s (m^3/kg_{free}) is the terrestrial ecotoxicity effect factor defined as PAF for the free ion form of the metal. We expressed the BF based on the free ion because calculation of the "truly" dissolved metal in soil requires input parameters that are rarely available, such as composition of major anions forming complexes with the free ion.

In the framework proposed by Gandhi et al.[2] for freshwater, the ACF is in practice part of the BF. The decoupling of the ACF from the BF for the soil assessment is recommended for two reasons. First, the ACF acknowledges the fact that the largest metal pool in soil is the solid-phase metal. Second, the ACF recognizes that not all forms of metal in soil are reactive. Others readily showed that dissolved concentrations of metals can be better predicted from the reactive metal pool instead of the total metal pool.[11-12] In freshwater, these aspects are expected to be less important because the particulate-bound metal fraction is often smaller than the total dissolved metal pool,[13] and because the reactivity of metal sorbed to suspended matter is not expected to be substantially reduced within time until it is removed by outflow and/or sedimentation.[14] The term "reactive" refers to the operational definition proposed by Degryse et al.[15] for the "labile" metal, given as metal in the solid phase that "equilibrates with the solution phase within a few days".

The terms accessibility and bioavailability are not new and have been used previously in the soil pollution context.[16-17] The ACF represents metal that is potentially able to cause ecotoxicity, i.e. metal which can partition to soil solution. This definition is consistent with that proposed by Reichenberg and Mayer[17] who define accessibility as "the mass quantity of a chemical that is or can become available within a given time span and under given conditions", and is fundamentally similar to that proposed earlier by Semple et al.[16] for bioaccessibility, which "encompasses what is actually bioavailable now plus what is potentially bioavailable". Mechanistically, our ACF is also consistent with the definition of bioaccessibility used in risk assessment of metals,[18-19] except that in the soil context the ACF refers to the partitioning in the natural instead of in the gastrointestinal environment. We find the term accessibility more appropriate as it represents metal pool potentially available for other processes than uptake by biota (as for example leaching from soil). The BF, expressed as a fraction of reactive metal, represents metal that is chemically active on its way to organisms (i.e. free ions), consistently with

Semple et al.[16] who defined the bioavailable compound “as that which is freely available to cross an organism’s cellular membrane from the medium the organism inhabits at a given time”. Note, that both the ACF and the BF are independent of the receptor, because the fate of the free ion within the organism after crossing the membrane does not depend on the soil anymore.

To illustrate these definitions with an example, the comparative toxicity potential of a metal will be the highest if all metal forms in soil are reactive and the only dissolved form are the free ions. However, even if the solid-phase metal is reactive and thus accessible within given time, metal can still become non bioavailable if speciation in soil pore water reduces concentration of the free ions to low levels (soil 1 in Fig. 1, left). On the other hand, even if the fraction of free ions in the solution is considerably large, the comparative toxicity potential of the metal can still be reduced if metal is not reactive because the total dissolved metal pool will be lower (soil 2 in Fig. 1, right). These two complementary sides of metal accessibility and bioavailability define exposure of terrestrial organisms through soil pore water and (in addition to fate and effects) are expected to control the magnitude of the comparative toxicity potential of metals in terrestrial systems.

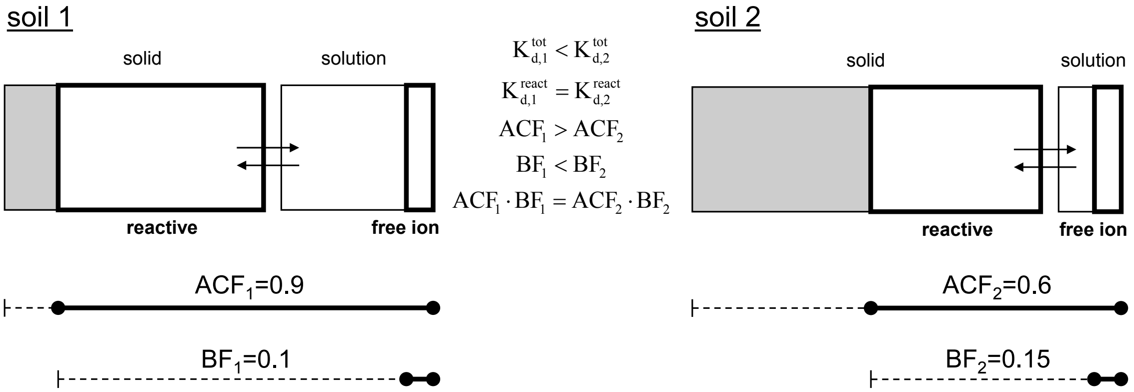

Fig. 1. The definitions of accessibility (ACF) and bioavailability (BF) factors in the proposed method for calculating CTPs of metals in soil (eq 2) illustrated for two hypothetical cases. K_d^{tot} is the distribution coefficient between total solid phase and solution phase; K_d^{react} is the distribution coefficient between reactive solid phase and solution phase. The grey box represents the metal pool that is not reactive, according to the definition given in the main text. The bold boxes represent reactive (solid) and free ion (solution) metal pools. The figure is not up to scale to make it more legible. In reality, the mass of metal in the solid phase is much larger than the mass of metal in the solution.[15] The figure is inspired by Fig. 1 in Degryse et al.[15]

2.2 Modeling Approach

Fate Factors. The fate factor ($FF_{i,s}$, day) represents the residence time of metal s in soil after emission to compartment i (eq 3). Note, that this definition of the FF includes a correction factor to acknowledge the fact that only a fraction of metal emitted to compartment i is transferred to soil, while the residence time of anthropogenically induced metal content in a soil refers to removal processes, such as leaching and runoff. We employed USEtox to calculate the FF of metal in natural soil after unit emission to continental rural air. USEtox is a consensus model developed through comparison and harmonization of seven LCIA-suited models and considers major fate mechanisms. Default USEtox environmental parameters were used combined with metal- and soil-specific K_d values. Calculations were performed for infinite time horizon, assuming instantaneous equilibrium for metal distribution and speciation. Similar approaches to modeling metal fate in soil have been presented previously.[20]

$$FF_{i,s} = \frac{\Delta C_{total,s} \cdot V \cdot \rho_b}{\Delta M_{s,i}} \quad (3)$$

where $\Delta C_{total,s}$ (kg_{total}/kg) is the incremental change in concentration of total metal s in soil; ΔM_s ($kg_{total\ emitted}/day$) is the incremental change in the emission of total metal s to compartment i; V (m^3) is the volume of the soil compartment; and ρ_b (kg/m^3) is the bulk density of the soil.

K_d, defined as the ratio between the concentration of total metal in the solid phase and the total dissolved metal was calculated employing empirical regression models recently proposed by Groenenberg et al.[21] Empirical regression models (see SI for a review) are equilibrium-based models and find application in deriving soil quality criteria[22] or in human exposure assessment.[23] The following criteria, listed in order of increasing priority, were applied to select models from available alternatives: (i) models with lower standard errors of estimate in soils outside the parameter range for which they were developed were preferred; (ii) models with lower standard errors of estimate in soils within the parameter range for which they were developed were preferred; (iii) models developed using soils spanning a wide range of environmental properties (pH, the content of organic carbon and total metal) were preferred; (iv) models developed using a large number of soils were preferred.

Due to the lack of measured values of the background content of Cu and Ni in each soil we assumed that they equal 14 and 16 mg/kg respectively. These values are median concentrations measured in European soils,[24] and were preferred over average (arithmetic mean) concentrations measured in the North America (25 and 19 mg/kg for Cu and Ni, respectively) [25] because the European set of soils is larger. It was moreover assumed that the content of amorphous, oxalate extractable Al and Fe (hydr)oxides ($AlFe_{ox}$) equals 89 mmol/kg. This value is the sum of median values for Al and Fe measured in Portuguese soils[26] and is close to the sum of median values measured in Dutch soils (44 and 24 mmol/kg for Fe and Al, respectively)[27]. The concentration of dissolved organic carbon (DOC) was estimated from pH, organic carbon and electrical conductivity using the regression model developed by Römkens et al.[28].

Accessibility Factors. The accessibility factor (ACF_s, $kg_{reactive}/kg_{total}$) of metal s in soil is proposed as:

$$ACF_s = \frac{\Delta C_{reactive}}{\Delta C_{total}} \quad (4)$$

where $\Delta C_{reactive}$ ($kg_{reactive}/kg$) is the incremental change of the concentration of reactive metal in soil; and ΔC_{total} (kg_{total}/kg) is the incremental change in concentration in total metal in soil. The ACF was calculated employing empirical regression models published by Römkens et al.[28] and Rodrigues et al.[26] (see SI). The same selection criteria were applied as for the selection of K_d regression model.

Bioavailability Factors. The bioavailability factor (BF_s, $kg_{free}/kg_{reactive}$) of metal s in soil was calculated as:

$$BF_s = \frac{\Delta C_{free} \cdot \theta_w}{\Delta C_{reactive} \cdot \rho_b} \quad (5)$$

where ΔC_{free} (kg_{free}/m^3) is the incremental change of the free ion fraction of metal; $\Delta C_{reactive}$ ($kg_{reactive}/kg$) is the incremental change in concentration in reactive metal content in soil; θ_w (m^3/m^3) is the volumetric soil water content. The BF was calculated using empirical regressions predicting the concentration of free metal ion from reactive metal published in Groenenberg et al.[27] (see SI). Again, the same selection criteria were applied as for the selection of K_d regression model.

Effect Factors. The effect factor (EF_s, m^3/kg_{free}) of metal s was calculated by assuming a constant value (= 0.5) for a linear dose-response function:[29]

$$EF_s = \frac{\Delta PAF}{\Delta C_{free}} = \frac{0.5}{HC50} \qquad (6)$$

where ΔPAF (dimensionless) is the incremental change in the potentially affected fraction of biological species in the soil ecosystem due to exposure to the free ion concentration of metal; and HC50 (kg_{free}/m^3) is the hazardous free ion concentration affecting 50% of the species, calculated as a geometric mean of free ion EC50 values for individual species.

Terrestrial biotic ligand models (TBLM) were chosen to calculate the EF because the fraction of metal bound to a biotic ligand of terrestrial organisms is expected to be a better descriptor of ecotoxicological response than activity of free ion in soil solution or total metal in soil.[4] Ecotoxicity models that in addition to competitive binding consider electrostatic interactions between metal ions and organism cells have been developed, but their availability is limited to plants.[30-31] The following criteria were used in selection of TBLMs: (i) models were selected to predict metal toxicity to organisms from at least three trophic levels (plants, microorganisms, and invertebrates); (ii) only models predicting chronic ecotoxicity were used (iii) only models developed in soils were used. The first two criteria were based on the recommended practice to use chronic EC50 values and the representation of the three fundamental trophic levels, both of which are essential to ensure the relevance of the calculated ecotoxicity indicators to terrestrial ecosystems.[32] The third criterion relates to the fact that most TBLMs have been developed in experimental model systems such as nutrient solutions or artificial porous media, and their applicability to soils has rarely been evaluated. Christiansen et al.[33] demonstrated how a biotic ligand model developed in nutrient solution fails to predict ecotoxicity of Cu to lettuce (*L. sativa*) when exposed in soil. In total, six models for Cu and Ni respectively,[4, 34] were selected (Table S3).

Soils. A global set of soils containing 760 topsoil profiles was selected from the ISRIC-WISE3 (version 3.1) soil database.[35-36] In total, the database holds data on measured soil properties for 10,253 soils collected in 149 countries.[36] The majority of soils were excluded from the modeling due to missing information on pH, organic carbon, clay, sand, silt, exchangeable cations and soil electrical conductivity (6608 cases). We also excluded 860 soils with soil electrical conductivity and exchangeable cations assigned "zero" values, because in those cases it was not possible to differentiate whether these parameters equaled "zero", or whether they were lacking values when accepting soil profile data to the database.[35] Another 1,331 profiles were excluded because the method used to measure soil electrical conductivity was either not specified, or it was stated that this parameter was not measured even when a value was assigned to this parameter (in most cases 0.1 dS/m). Because the TBLMs are not applicable to calcareous soils, soils with carbonate content ($CaCO_3$) above 0% (437 cases) and those with pH>6.5 that did not have a value assigned to $CaCO_3$ (252 cases), were also excluded. To the remaining soils that did not report $CaCO_3$, a value of 0% was assigned (57 cases). Finally, saline soils (ionic strength of soil pore water above 0.5 mol/l) were not included because of uncertainties related to calculations of ion activity coefficients (5 cases). This resulted in 760 noncalcareous soils for which CTPs could be calculated. These soils span a wide range of properties with respect to the most influential parameters affecting metal bioavailability and ecotoxicity, i.e. pH, content of organic carbon, and ionic composition of soil pore water (Table S1). Note that the latter is not given in the database and was calculated following the Gaines-Thomas convention for modeling cation exchange, as presented in the SI. The location of those soils for which geographical references are available is shown in Fig. S1.

Multiple Linear Regression Analysis. Based on the individual soil CTPs, we developed multiple linear regression (MLR) models to analyze the influence of soil properties controlling the CTP (eq 7). They can be used to calculate CTPs directly from soil parameters. The MLR models were also derived to analyze the influence of soil properties controlling each model constituent in eq 2 (see SI). Only those soil parameters which were included in models used to calculate K_d values, concentrations of reactive, total dissolved, and free metal ions (eq S6-S22) were selected as independent variables. Some parameters were excluded due to strong (r>0.8; r=Pearson correlation coefficient) correlation with other parameters (see SI for details).

$$\log_{10}(CTP) = a + b \cdot pH + c \cdot \log_{10}(ORGC) + d \cdot \log_{10}\left(\left[Mg^{2+}\right]\right) + e \cdot \log_{10}(CLAY) \tag{7}$$

where CTP ($m^3/kg_{\text{total emitted to air}} \cdot day$) is the comparative toxicity potential of total metal emitted to air; ORGC (%) is the organic carbon, $[Mg^{2+}]$ (mol/l) is magnesium concentration in soil pore water; and CLAY (%) is clay content.

The coefficients of eq 7 were derived in IBM SPSS Statistics 20 (IBM Corp., Armonk, NY) using values calculated for the whole set of 760 soils, and were included in the regression if they passed stepping criteria ($p<0.05$ for entry, and $p>0.1$ for removal) and were significant at the probability level $p<0.001$.

Normalized Sensitivity Coefficients. Sensitivity of CTPs to uncertain model parameters was analyzed by computing normalized sensitivity coefficients (eq 8), as done in Prommer et al.:[37]

$$X_{CTP,k} = \frac{\Delta CTP / CTP}{\Delta a_k / a_k} \tag{8}$$

where $X_{CTP,k}$ is the normalized sensitivity coefficient of CTP for perturbance of parameter k, a_k is the k^{th} parameter value, Δa_k is the perturbation of parameter a_k, CTP is the calculated comparative toxicity potential, and ΔCTP is the change of the comparative toxicity potential that resulted from the perturbation of parameter a_k. Note, that in Prommer et al. their analysis was done using constant value of the Δa_k (10%). Here the Δa_k vary between the parameters, and is chosen based on the realistic ranges of uncertain model parameters.

3. Results and Discussion

Below, we present results for CTP and each model constituent in eq 2 for a unit emission of Cu and Ni to air. Geographic variability of CTPs accompanied by sensitivity analysis, consideration of method limitations, and a presentation of implications for LCIA, are then discussed.

K_d values. Median (95% geographic variability intervals) values of K_d are 9.1×10^2 ($2\times10^2 - 2.5\times10^3$) and 1.8×10^3 ($6.2\times10^2 - 4.1\times10^3$) l/kg for Cu and Ni, respectively (Fig. 2a). They are within ranges of measured values for different soils.[15] If more detailed data on soil characteristics, such as type and properties of organic matter and soil minerals become available, equilibrium multisurface models may be preferred over empirical regressions to obtain more precise values of partitioning coefficients.[38-39]

Fate Factors. Median (95% geographic variability intervals) values of FFs are 3.9×10^4 (1.4×10^4 – 1.9×10^4) and 7.1×10^4 (2.7×10^4 – 1.3×10^5) days for Cu and Ni, respectively (Fig. 2b). Organic carbon and pH are the major soil properties controlling K_d values and consequently FFs of Cu and Ni, respectively (Table S8). Fate factor increases with increase in the partitioning coefficient, which is explained by the latter's strong influence on processes included in the fate model, i.e. leaching to deeper soil layers and runoff from soil (Fig. S6). These processes are slow for metals due to their strong binding to soil constituents, resulting in residence times of hundreds of years for a soil layer of 0.1 m. Soil erosion becomes however an important removal process in those soils in which K_d values are very high. As a consequence, FFs level off at high K_d values. USEtox predicts that ~1000 years is required for all soil to become eroded to surface water; soil erosion thus determines the maximum residence time of a metal in soil. Residence times in range of hundreds of years indicate that some impacts will be excluded if finite time horizons are chosen in modeling comparative toxicity potentials.[40]

Accessibility Factors. Median (95% geographic variability intervals) values of ACFs equal 0.42 (0.35 – 0.65) and 0.06 (0.022 – 0.13) $kg_{reactive}/kg_{total}$ for Cu and Ni, respectively (Fig. 2c). In none of the 760 soils is the reactive fraction equal to 1, as is assumed in current LCIA practice. [41] This is an important aspect to consider because even if metal is initially reactive, the reactive fraction in soil can decrease significantly at time scales of months[42], reducing the magnitude of CTPs. Here, we assume that the reactive metal is in equilibrium with total metal. This assumption can be justified because the regression models used to calculate reactive metal have been derived from both uncontaminated and contaminated, aged soils. The calculated median value of the reactive fraction of Cu is close to the median value measured in soils from 19 paddy fields of Taiwan (0.56),[12] but is higher than median value measured in 136 soils from Portugal (0.2).[26] By contrast, median reactive fraction for Ni (calculated using the regression developed for the Portuguese soils) is lower than the median value measured in the Taiwanese soils (0.23). The difference can be attributed to the fact that both Dutch and Taiwanese soils have been formed from unconsolidated river sediments of different properties than soils formed from parent material, such as the Portuguese ones. As noted by Römkens et al.[28] the fraction of reactive metal will be lower in soils derived from parent material, because a larger proportion of metal is included in non-reactive minerals. The reactive fraction of Cu and Ni predicted by the kinetic model of Crout et al.[43] using kinetic parameters from Buekers et al.[42] for pH 5.7 (median for soils) and infinite time equal to 0.6 and 0.65, respectively. These values are higher than median values calculated here, which may be clarified by the fact that the model of Buekers et al. does not capture those processes which occur after ~800 days in soil, such as precipitation of salts and formation of minerals.[44] If more information on the type of reactive surfaces and kinetics of reactions becomes available, assemblage models constructed using multisurface models can be employed for modeling both speciation in soil pore water and time-dependent changes in the solid-phase metal reactivity in soils.[42]

Our study corroborates earlier study recommending the use of calibrated bioavailability models to correct for metal leaching and aging[45] by introducing a factor which is based on a mechanistic understanding of processes affecting metal availability in soils. Further work should be devoted to considerations of changes in metal reactivity with time as affected by emitted forms of metal and soil properties. This aspect is particularly relevant if finite time horizons are considered in modeling comparative toxicity potentials for metals.

The ACF is not just relevant for metals in soil. The availability of some organic contaminants can also be reduced in soil by sorption to organic matter and slow diffusion into micropores.[46] Indeed, the truly dissolved concentration and bioaccumulation of some hydrophobic organic compounds are better predicted if sorption to carbonaceous materials such as black carbon, coal, and kerogen (collectively called “carbonaceous geosorbents”, GC) constituting approximately 10% of total organic carbon is taken into account.[47] As for metals fixed in soil, the majority of GC-bound hydrophobic organics is resistant to release.[47] The ACF can be applied to capture the differences in availability in such cases. Then, the BF (for organics known as the exposure factor, XF) can be used to translate between the compound available for partitioning and the truly dissolved fraction, as is practiced today.[48] If a compound does not bind strongly to the GC, the ACF=1, and the BF is a sufficient descriptor of the exposure through soil pore water.

Bioavailability Factors. Median (95% geographic variability intervals) values of BFs equal 2.3×10^{-6} (1.7×10^{-7} – 4.8×10^{-5}) and 6.8×10^{-4} (1.6×10^{-4} – 3.3×10^{-3}) $\text{kg}_{\text{free}}/\text{kg}_{\text{reactive}}$ for Cu and Ni, respectively (Fig. 2d). To test the accuracy of these predictions, we calculated the concentrations of free metal ions expressed as a fraction of total dissolved metal using regression models employed to calculate concentration of free ion and total dissolved metal, and compared them with the free ion fraction of total dissolved metal measured by others. The free Cu^{2+} fraction of total dissolved Cu ranges 4.6 orders of magnitude (Fig. S8) and decreases with soil pH (data not shown). This is confirmed by measurements in soil solutions from various soils.[15, 27] The lowest fraction of free Cu^{2+} measured by Groenenberg et al.[27] (3×10^{-7}) is about 2 orders of magnitude lower than the lowest value calculated here (5.4×10^{-5}), while the lowest value calculated here for Ni^{2+} (1.6×10^{-1}) does not reach the lowest value measured by Groenenberg et al. [27] (2×10^{-2}). This is because only five soils with pH>7 and only two soils with organic carbon content above 20%, in which bioavailability of Cu and Ni is expected to be low, were included in our data set. Here, in one soil the calculated free ion fraction of total dissolved Cu exceeds the maximum possible value of 1 (by 129%), while the fraction of free Ni^{2+} exceeds the maximum possible value of 1 in five soils (by<12%). We consider these predictions as sufficiently accurate to incorporate the BFs in calculations of CTPs.

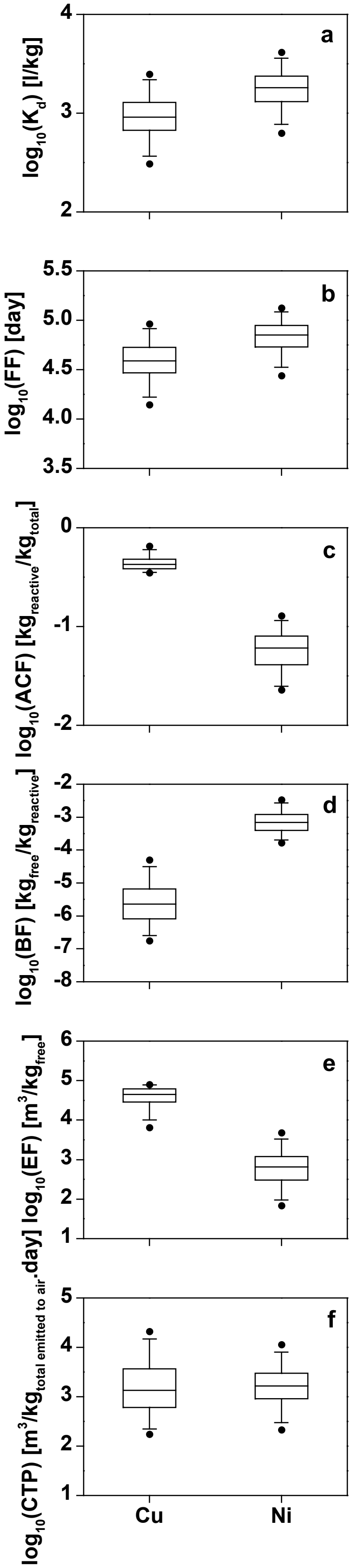

Fig 2. Log_{10}-transformed K_d values (a), FFs (b), ACFs (c), BFs (d), EFs (e) and CTPs (f) for Cu and Ni calculated for 760 soils. Boxes with bars indicate the 5th, 25th, 50th, 75th and 95th percentiles; black dots indicate 2.5th and 97.5th percentiles of the calculated values.

Effect Factors. Median (95% geographic variability intervals) values of EFs are 4.4×10^4 (6.4×10^3 – 7.8×10^4) and 6.6×10^2 (6.7×10^1 – 4.7×10^3) m^3/kg_{free} for Cu and Ni, respectively (Fig. 2e). EFs of Ni span a wider range than those for Cu, because in all cases, except of nitrifying microorganisms, only protons compete with Cu^{2+} for binding to biotic ligands, whereas the toxicity of Ni^{2+} is also alleviated by Mg^{2+}, and sometimes by Ca^{2+}. As a consequence, EFs of Cu strongly correlate with soil pH (Table S11). In contrast, the EF of Ni primarily correlates with the concentration of Mg^{2+} dissolved in soil pore water. Comparison between our species sensitivity distributions (SSD) constructed from the TBLM-derived EC50 values, and SSDs derived from species effect data from ecotoxicity experiments shows that even though non-alkaline soils dominate our dataset, and there are differences in species included in the comparison, in many cases our SSDs fall within the 95% confidence interval for the experimental SSD (see SI). We consider these predictions as reasonable and sufficiently accurate to employ our EFs for calculating CTPs.

Haye et al.[49] showed that EF based on total metal for Cu was 3.2 times higher than that for Ni. Here, the ecotoxicity ranking of Cu and Ni is more similar to what was observed for freshwater organisms by Gandhi et al.[2] who showed that Cu is about 80 times more toxic than Ni when the EF was based on the "truly" dissolved metal. Toxicity of metals can be related to the strength of their binding to biomass, such as plasma membranes, cell walls, and proteins, and has been shown to correlate with metal softness.[50-51] A property of soft metals is that they have strong binding affinity to soft ligands, such as biomass. If corrected for differences in ionic composition of the environment, only molecular properties of metal ions and the type of biomass will drive the metal uptake and toxicity, which may explain the similarities reported here between toxicity ranking of metal ions for terrestrial and aquatic organisms. Veltman et al.[52-53] have already demonstrated that the absorption rate constant and the conditional affinity constant of various aquatic species were positively correlated with the metal covalent index.

Comparative Toxicity Potentials. Comparative Toxicity Potentials range 3.5 and 3 orders of magnitude for Cu and Ni, respectively, with median values (95% geographic variability intervals) equal to 1.7×10^2 (1.7×10^1 – 2×10^4) and 1.7×10^3 (2.1×10^2– 1.1×10^4) $m^3/kg_{\text{total emitted to air to air}}\cdot$day. They are distributed lognormally (see SI).

Multiple linear regressions show that the CTP of Cu is determined mainly by soil organic carbon (Table 1), influencing metal fate. The predictive power of the equation for calculating CTPs of Cu is improved by including the effects of soil pH, influencing bioavailability (Table S10). In contrast to Cu, the compensating effects of soil organic carbon on both accessibility and bioavailability result in soil organic carbon being a rather poor descriptor of CTP for Ni. The CTP of Ni is mainly controlled by pore water concentration of Mg^{2+}, through its influence on ecotoxicity. This poses a challenge for global scale modeling of ecotoxic impacts from those metals for which base cations alleviate toxicity to soil organisms, because pore water concentrations of Mg^{2+} and other base cations are neither routinely measured, nor are they specific to soil types.[54] As demonstrated here, however, they can be calculated from electrical conductivity of soil pore water, which can be measured or estimated from soil properties.[55]

Table 1. Linear regression coefficients, adjusted R^2 values (R^2_{adj}) and standard error of estimate (se) of regression equations for $\log_{10}$(CTP) of Cu and Ni (eq 7). Values in brackets indicate standard error.

Metal	a intercept	B pH	C $\log_{10}$(ORGC)	d $\log_{10}([Mg^{2+}])$	e $\log_{10}$(CLAY)	R^2_{adj}	se
Cu	3.327 (0.010)	x	-1.003 (0.019)	x	x	0.784	0.27
	5.653 (0.038)	-0.408 (0.007)	-1.150 (0.008)	x	x	0.965	0.11
	6.006 (0.039)	-0.426 (0.006)	-1.166 (0.007)	0.072 (0.005)	x	0.973	0.093
	6.074 (0.043)	-0.427 (0.006)	-1.156 (0.007)	0.078 (0.005)	-0.035 (0.009)	0.974	0.092
Ni	1.540 (0.037)	x	x	-0.482 (0.010)	x	0.736	0.22
	1.613 (0.033)	x	-0.209 (0.014)	-0.470 (0.009)	x	0.795	0.19
	0.962 (0.079)	0.104 (0.012)	-0.169 (0.014)	-0.486 (0.009)	x	0.815	0.19
	0.701 (0.083)	0.107 (0.011)	-0.209 (0.015)	-0.510 (0.009)	0.134 (0.017)	0.828	0.18

CTP ($m^3/kg_{total\ emitted\ to\ air\ to\ air}\cdot day$) is the comparative toxicity potential of total metal emitted to air; ORGC (%) is the organic carbon content; $[Mg^{2+}]$ (mol/l) is magnesium concentration in soil pore water; and CLAY (%) is the clay content; x indicates that the variable did not pass stepping method criteria ($p<0.05$ for entry, and $p>0.1$ for removal); all coefficients are significant at the probability level $p<0.001$.

Sensitivity Analysis. The sensitivity of CTPs to many model parameters is metal- and soil-specific (Fig. 3). The parameters affecting ionic composition of soil pore water (such as the Gaines-Thomas selectivity coefficients for cation exchange, K^{GT}) appear important for Ni due to competitive binding of Mg^{2+} to biotic ligands. However, if the full set of three K^{GT} values is in lower and higher range of values typical for clay soils (Table S15), median CTPs of Ni change by 4 and 5%, respectively, compared with the base scenario (data not shown). The influence of soil moisture on CTPs of Ni is larger compared to Cu because concentration of dissolved Mg^{2+} is also proportional to the water content (eq S1), whereas the precipitation rate can influence CTP of both Cu and Ni due to its control of leaching and runoff. The geographic variability in the CTP of Cu is expected to be higher if data on location-specific content of amorphous Fe and Al (hydr)oxides were available.

The CTPs for both metals are more sensitive to low background metal content, compared with high background levels. However, using a European subset of 24 soils (see SI for details) we show that median CTPs change by 10% for both metals if location-specific background metal is used instead of constant values. For the same subset, an increase in reactive metal to the levels expected in soils from paddy fields of Taiwan (56 and 23% of total, location-specific Cu and Ni, respectively)[12] is to some extent compensated by shorter residence time of a metal. However, a 10% change in K_d or DOC will result in nearly 10% change in CTPs, due to their influence on metal fate. Overall, it can be concluded that inclusion of location-specific model parameters will improve accuracy of soil-specific CTPs and will probably increase geographic variability in the CTPs, but is not expected to considerably (<10%) influence median values, at least at a global scale. If a regionalized assessment at country levels is to be performed, attention must be paid to the dependency of CTPs on soil moisture and precipitation rates.

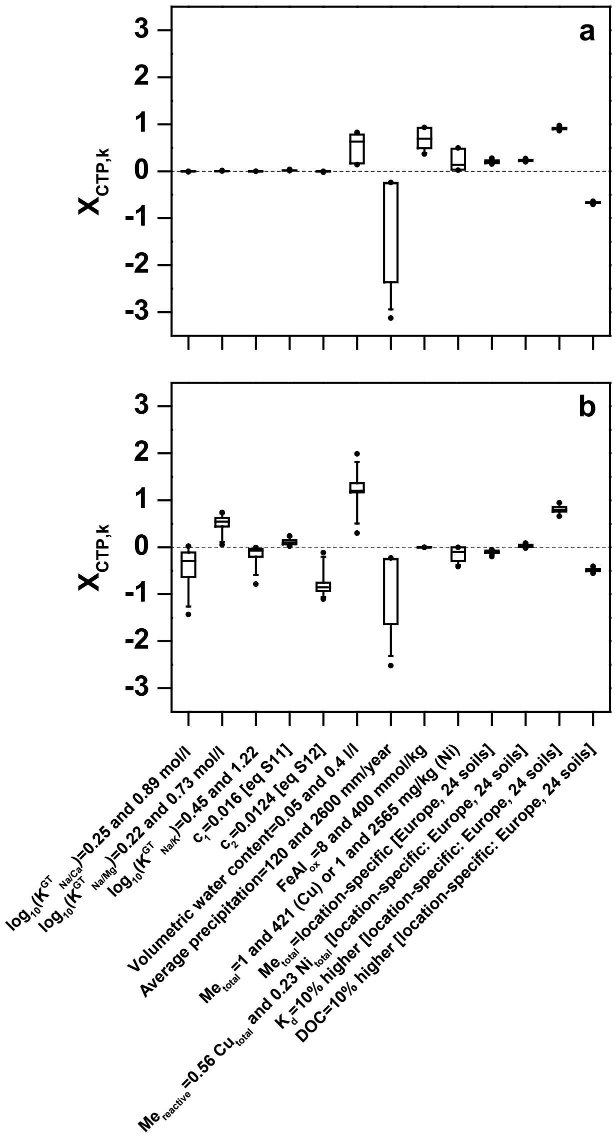

Fig. 3. Normalized sensitivity coefficients ($X_{CTP,k}$) computed using eq 8 for several uncertain model parameters with respect to the calculated CTPs of Cu (a) and Ni (b) in all 760 soils, or in the European subset of 24 soils. Boxes with bars indicate the 5th, 25th, 50th, 75th and 95th percentiles; black dots indicate 2.5th and 97.5th percentiles of the calculated values. Details on selection of K^{GT} values and location-specific background metal content are given in the SI.

Method Limitations. We propose a new method for calculating CTPs of Cu and Ni in soil, but its extension to other metals or terrestrial systems can be limited. Multisurface speciation models can be applied to metals lacking empirical regressions, and terrestrial free ion activity models (FIAM), or freshwater ecotoxicity EFs can be adapted to cover metals lacking TBLMs. Alternatively, quantitative ion character-activity relationships (QICAR) can be developed, as done for freshwater organisms.[56] The coverage of saline and calcareous soils will be challenged by the need for validating existing speciation and ecotoxicity models.

Our method does not capture the aspects of metal essentiality, active plant uptake, or microbial adaptation, but it is not obvious how these limitations affect toxicity potentials. Whereas toxic pressure has been demonstrated to relate to biodiversity,[57-58] positive effects on a species level might not always translate into positive effects on an ecosystem level.[59]

It should be also noted that research is needed to evaluate whether the framework can be applied to elements forming anions or organic compounds, whereas the reactivity of massive metal products and metallic nanoparticles is expected to be more dependent on the particle size and/or shape than on the initial chemical form.[60-62]

Finally, we stress that LCIA-suited models are based on an average situation that is appropriate to rank substances according to their toxicity potential for application in LCA. However, environmental risk assessment (ERA) or environmental impact assessment (EIA) usually operate in well-defined settings, and practitioners thus should consider employing site specific fate and exposure models to (ideally) best represent conditions at a site. For example, if our method is used to calculate CTP for a metal emitted directly to an agricultural soil, metal removal via plant harvest can play a role in determining metal fate.[63]

Practical Implications. Our new CTPs of Ni and Cu in soils, taking metal accessibility into account, highlight the need for considering variability in soil properties as drivers of metal CTPs. These aspects of terrestrial ecotoxicity assessment of metals are not included yet in the existing LCIA methodologies.[41] For applications in regionalized assessments, it is important to evaluate the variability of CTPs as controlled by spatially variable soil properties. The scientifically relevant spatial scales can be different for different metals, due to differences in variability of soil parameters controlling CTPs, as demonstrated here for Cu and Ni. In situations where the emission location is unknown, as is often the case in LCA, it is important to carefully select generic values of CTPs. Weighting of CTPs can be done based on the relative occurrence of soils. Alternatively, soil archetypes can be derived for which spatially-determined variability of CTPs can be calculated. In both cases, our empirical CTP-regression can be directly employed to calculate CTPs for Cu and Ni from soil parameters.

Associated Content

Supporting Information. Location and properties of soils; methodology for calculation of ionic composition of soil pore water; a review and selection of empirical regression models; structure, parameters, and predictions of TBLMs; multiple linear regressions analysis; details on the sensitivity analysis; and additional results.

Acknowledgements

We appreciate stimulating discussions about metal pools in soil with Ole K. Borggaard, Peter E. Holm, and Karen S. Christiansen (Department of Basic Sciences and Environment, University of Copenhagen). We also acknowledge Ole K. Borggaard and Rasmus Jakobsen (DTU Environment) for their suggestions related to modeling of cation exchange, and Alexis Laurent (DTU Management Engineering) for the comments on an earlier version of the manuscript. This research was funded by the European Commission under the 7th framework program on environment; ENV.2009.3.3.2.1: LC-IMPACT – development and application of environmental Life Cycle Impact assessment Methods for imProved sustAinability Characterization of Technologies, grant agreement 243827.

References

1. Diamond, M. L.; Gandhi, N.; Adams, W. J.; Atherton, J.; Bhavsar, S. P.; Bulle, C.; Campbell, P. G. C.; Dubreuil, A.; Fairbrother, A.; Farley, K.; Green, A.; Guinee, J.; Hauschild, M. Z.; Huijbregts, M. A. J.; Humbert, S.; Jensen, K. S.; Jolliet, O.; Margni, M.; McGeer, J. C.; Peijnenburg, W.; Rosenbaum, R.; van de Meent, D.; Vijver, M. G., The clearwater consensus: the estimation of metal hazard in fresh water. *Int. J. Life Cycle Assess.* **2010,** *15*, (2), 143-147.
2. Gandhi, N.; Diamond, M. L.; van de Meent, D.; Huijbregts, M. A. J.; Peijnenburg, W. J. G. M.; Guinée, J., New method for calculating comparative toxicity potential of cationic metals in freshwater: application to copper, nickel, and zinc. *Environ. Sci. Technol.* **2010,** *44*, (13), 5195-5201.
3. Oorts, K.; Ghesquiere, U.; Swinnen, K.; Smolders, E., Soil properties affecting the toxicity of CuCl2 and NiCl2 for soil microbial processes in freshly spiked soils. *Environ. Toxicol. Chem.* **2006,** *25*, (3), 836-844.
4. Thakali, S.; Allen, H. E.; Di Toro, D. M.; Ponizovsky, A. A.; Rooney, C. P.; Zhao, F.-J.; McGrath, S. P., A terrestrial biotic ligand model. 1. Development and application to Cu and Ni toxicities to barley root elongation in soils. *Environ. Sci. Technol.* **2006,** *40*, (22), 7085-7093.
5. Sauvé, S.; Hendershot, W.; Allen, H. E., Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environ. Sci. Technol.* **2000,** *34*, (7), 1125-1131.
6. Degryse, F.; Buekers, J.; Smolders, E., Radio-labile cadmium and zinc in soils as affected by pH and source of contamination. *Eur. J. Soil Sci.* **2004,** *55*, (1), 113-121.
7. Reuter, H. I.; Lado, L. R.; Hengl, T.; Montanarella, L., Continental-scale digital soil mapping using European soil profile data: soil pH. *Hamburger Beiträge zur Physischen Geographie und Landschaftsökologie* **2008,** *19*, 91-102.
8. Hauschild, M. Z.; Huijbregts, M.; Jolliet, O.; MacLeod, M.; Margni, M.; van de Meent, D. V.; Rosenbaum, R. K.; McKone, T. E., Building a model based on scientific consensus for life cycle impact assessment of chemicals: The search for harmony and parsimony. *Environ. Sci. Technol.* **2008,** *42*, (19), 7032-7037.
9. Rosenbaum, R. K.; Bachmann, T. M.; Gold, L. S.; Huijbregts, M. A. J.; Jolliet, O.; Juraske, R.; Koehler, A.; Larsen, H. F.; MacLeod, M.; Margni, M.; McKone, T. E.; Payet, J.; Schuhmacher, M.; van de Meent, D.; Hauschild, M. Z., USEtox-the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *Int. J. Life Cycle Assess.* **2008,** *13*, (7), 532-546.
10. Nicholson, F. A.; Smith, S. R.; Alloway, B. J.; Carlton-Smith, C.; Chambers, B. J., An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci Total Environ* **2003,** *311*, (1-3), 205-219.
11. Degryse, F.; Broos, K.; Smolders, E.; Merckx, R., Soil solution concentration of Cd and Zn can be predicted with a CaCl2 soil extract. *Eur. J. Soil Sci.* **2003,** *54*, (1), 149-157.
12. Romkens, P. F.; Guo, H.-Y.; Chu, C.-L.; Liu, T.-S.; Chiang, C.-F.; Koopmans, G. F., Characterization of soil heavy metal pools in paddy fields in Taiwan: chemical extraction and solid-solution partitioning. *J. Soils Sediments* **2009,** *9*, (3), 216-228.
13. Popp, M.; Koellensperger, G.; Stingeder, G.; Hann, S., Novel approach for determination of trace metals bound to suspended solids in surface water samples by inductively coupled plasma sector field mass spectrometry (ICP-SFMS). *J Anal At Spectrom* **2008,** *23*, (1), 111-118.
14. Garnier, J. M.; Ciffroy, P.; Benyahya, L., Implications of short and long term (30 days) sorption on the desorption kinetic of trace metals (Cd, Zn, Co, Mn, Fe, Ag, Cs) associated with river suspended matter. *Sci Total Environ* **2006,** *366*, (1), 350-360.

15. Degryse, F.; Smolders, E.; Parker, D. R., Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications - a review. *Eur. J. Soil Sci.* **2009,** *60*, (4), 590-612.

16. Semple, K. T.; Doick, K. J.; Jones, K. C.; Burauel, P.; Craven, A.; Harms, H., Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. *Environ. Sci. Technol.* **2004,** *38*, (12), 228A-231A.

17. Reichenberg, F.; Mayer, P., Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environ. Toxicol. Chem.* **2006,** *25*, (5), 1239-1245.

18. Peijnenburg, W. J. G. M.; Jager, T., Monitoring approaches to assess bioaccessibility and bioavailability of metals: Matrix issues. *Ecotoxicol. Environ. Saf.* **2003,** *56*, (1), 63-77.

19. Ruby, M. V.; Schoof, R.; Brattin, W.; Goldade, M.; Post, G.; Harnois, M.; Mosby, D. E.; Casteel, S. W.; Berti, W.; Carpenter, M.; Edwards, D.; Cragin, D.; Chappell, W., Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environ. Sci. Technol.* **1999,** *33*, (21), 3697-3705.

20. Bhavsar, S. P.; Gandhi, N.; Diamond, M. L., Extension of coupled multispecies metal transport and speciation (TRANSPEC) model to soil. *Chemosphere* **2008,** *70*, (5), 914-924.

21. Groenenberg, J. E.; Dijkstra, J. J.; Bonten, L. T. C.; de Vries, W.; Comans, R. N. J., Evaluation of the performance and limitations of empirical partition-relations and process based multisurface models to predict trace element solubility in soils. *Environ. Pollut.* **2012,** *166*, (0), 98-107.

22. Lofts, S.; Spurgeon, D. J.; Svendsen, C.; Tipping, E., Deriving soil critical limits for Cu, Zn, Cd, and Ph: A method based on free ion concentrations. *Environ. Sci. Technol.* **2004,** *38*, (13), 3623-3631.

23. Pizzol, M.; Bulle, C.; Thomsen, M., Indirect human exposure assessment of airborne lead deposited on soil via a simplified fate and speciation modelling approach. *Sci Total Environ* **2012,** *421–422*, (0), 203-209.

24. Lado, L. R.; Hengl, T.; Reuter, H. I., Heavy metals in European soils: A geostatistical analysis of the FOREGS Geochemical database. *Geoderma* **2008,** *148*, (2), 189-199.

25. Shacklette, H. T.; Boerngen, J. G. *Element concentration in soils and other surficial materials of the conterminous United States.*; USGS (United States Geological Survey) professional paper 1270: 1984.

26. Rodrigues, S. M.; Henriques, B.; da Silva, E. F.; Pereira, M. E.; Duarte, A. C.; Romkens, P., Evaluation of an approach for the characterization of reactive and available pools of twenty potentially toxic elements in soils: Part I - The role of key soil properties in the variation of contaminants' reactivity. *Chemosphere* **2010,** *81*, (11), 1549-1559.

27. Groenenberg, J. E.; Römkens, P. F. A. M.; Comans, R. N. J.; Luster, J.; Pampura, T.; Shotbolt, L.; Tipping, E.; De Vries, W., Transfer functions for solid-solution partitioning of cadmium, copper, nickel, lead and zinc in soils: derivation of relationships for free metal ion activities and validation with independent data. *Eur. J. Soil Sci.* **2010,** *61*, (1), 58-73.

28. Römkens, P. F. A. M.; Groenenberg, J. E.; Bonten, L. T. C.; Vries, W. d.; Bril, J. *Derivation of partition relationships to calculate Cd, Cu, Ni, Pb, Zn solubility and activity in soil solutions*; Alterra: Wageningen, 2004; p 75.

29. Pennington, D. W.; Payet, J.; Hauschild, M., Aquatic ecotoxicological indicators in life-cycle assessment. *Environ. Toxicol. Chem.* **2004,** *23*, (7), 1796-1807.

30. Wang, P.; De Schamphelaere, K. A. C.; Kopittke, P. M.; Zhou, D. M.; Peijnenburg, W.; Lock, K., Development of an electrostatic model predicting copper toxicity to plants. *J Exp Bot* **2012,** *63*, (2), 659-668.

31. Wang, P.; Kinraide, T. B.; Zhou, D.; Kopittke, P. M.; Peijnenburg, W. J. G. M., Plasma membrane surface potential: dual effects upon ion uptake and toxicity. *Plant Physiol* **2011,** *155*, (2), 808-820.

32. EC *Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market*; Joint Research Centre, European Chemicals Bureau: Brussels, Belgium, 2003.

33. Christiansen, K. S.; Borggaard, O. K.; Holm, P. E.; Vijver, M. G.; Hauschild, M. Z.; Peijnenburg, W. J. G. M., Does the biotic ligand model approach improve the effect assessment of copper for plants in soil? *Environ. Toxicol. Chem.* **2012**.

34. Thakali, S.; Allen, H. E.; Di Toro, D. M.; Ponizovsky, A. A.; Rooney, C. P.; Zhao, F.-J.; McGrath, S. P.; Criel, P.; Van Eeckhout, H.; Janssen, C. R.; Oorts, K.; Smolders, E., Terrestrial biotic ligand model. 2. Application to Ni and Cu toxicities to plants, invertebrates, and microbes in soil. *Environ. Sci. Technol.* **2006,** *40*, (22), 7094-7100.

35. Batjes, N. H. *ISRIC-WISE harmonized global soil profile dataset (version 3.1)*; 2008 ⁄ 02; ISRIC –World Soil Information: Wageningen, 2008.

36. Batjes, N. H., Harmonized soil profile data for applications at global and continental scales: updates to the WISE database. *Soil Use and Management* **2009,** *25*, (2), 124-127.

37. Prommer, H.; Tuxen, N.; Bjerg, P. L., Fringe-controlled natural attenuation of phenoxy acids in a landfill plume: integration of field-scale processes by reactive transport modeling. *Environ. Sci. Technol.* **2006,** *40*, (15), 4732-4738.

38. Dijkstra, J. J.; Meeussen, J. C. L.; Comans, R. N. J., Leaching of heavy metals from contaminated soils: An experimental and modeling study. *Environ. Sci. Technol.* **2004,** *38*, (16), 4390-4395.

39. Dijkstra, J. J.; Meeussen, J. C. L.; Comans, R. N. J., Evaluation of a generic multisurface sorption model for inorganic soil contaminants. *Environ. Sci. Technol.* **2009,** *43*, (16), 6196-6201.

40. Huijbregts, M. A. J.; Guinee, J. B.; Reijnders, L., Priority assessment of toxic substances in life cycle assessment. III: Export of potential impact over time and space. *Chemosphere* **2001,** *44*, (1), 59-65.

41. Pizzol, M.; Christensen, P.; Schmidt, J.; Thomsen, M., Eco-toxicological impact of "metals" on the aquatic and terrestrial ecosystem: A comparison between eight different methodologies for Life Cycle Impact Assessment (LCIA). *Journal of Cleaner Production* **2011,** *19*, (6-7), 687-698.

42. Buekers, J.; Degryse, F.; Maes, A.; Smolders, E., Modelling the effects of ageing on Cd, Zn, Ni and Cu solubility in soils using an assemblage model. *Eur. J. Soil Sci.* **2008,** *59*, (6), 1160-1170.

43. Crout, N. M. J.; Tye, A. M.; Zhang, H.; McGrath, S. P.; Young, S. D., Kinetics of metal fixation in soils: Measurement and modeling by isotopic dilution. *Environ. Toxicol. Chem.* **2006,** *25*, (3), 659-663.

44. Amacher, M., Methods for obtaining and analyzing kinetic data. In *Rates of soil chemical processes* Sparks, D. L.; Suarez, D. L., Eds. Soil Science Society of America: Madison, WI, 1991; Vol. Special Publication no. 27, pp 19-59.

45. Smolders, E.; Oorts, K.; van Sprang, P.; Schoeters, I.; Janssen, C. R.; McGrath, S. P.; McLaughlin, M. J., Toxicity of trace metals in soil as affected by aoil type and aging after contamination: using calibrated bioavailability models to set ecological soil standards. *Environ. Toxicol. Chem.* **2009,** *28*, (8), 1633-1642.

46. Alexander, M., Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ. Sci. Technol.* **2000,** *34*, (20), 4259-4265.

47. Cornelissen, G.; Gustafsson, O.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; Van Noort, P. C. M., Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and

soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* **2005,** *39*, (18), 6881-6895.

48. Henderson, A.; Hauschild, M.; van de Meent, D.; Huijbregts, M.; Larsen, H.; Margni, M.; McKone, T.; Payet, J.; Rosenbaum, R.; Jolliet, O., USEtox fate and ecotoxicity factors for comparative assessment of toxic emissions in life cycle analysis: sensitivity to key chemical properties. *The International Journal of Life Cycle Assessment* **2011,** *16*, (8), 701-709.

49. Haye, S.; Slaveykova, V. I.; Payet, J., Terrestrial ecotoxicity and effect factors of metals in life cycle assessment (LCA). *Chemosphere* **2007,** *68*, (8), 1489-1496.

50. Kinraide, T. B.; Yermiyahu, U., A scale of metal ion binding strengths correlating with ionic charge, Pauling electronegativity, toxicity, and other physiological effects. *J Inorg Biochem* **2007,** *101*, (9), 1201-1213.

51. Kinraide, T. B., Improved scales for metal ion softness and toxicity. *Environ. Toxicol. Chem.* **2009,** *28*, (3), 525-533.

52. Veltman, K.; Huijbregts, M. A. J.; Hendriks, A. J., Integration of biotic ligand models (BLM) and bioaccumulation kinetics into a mechanistic framework for metal uptake in aquatic organisms. *Environ. Sci. Technol.* **2010,** *44*, (13), 5022-5028.

53. Veltman, K.; Huijbregts, M. A. J.; Van Kolck, M.; Wang, W. X.; Hendriks, A. J., Metal bioaccumulation in aquatic species: Quantification of uptake and elimination rate constants using physicochemical properties of metals and physiological characteristics of species. *Environ Sci Technol* **2008,** *42*, (3), 852-858.

54. Mertens, F. M.; Paetzold, S.; Welp, G., Spatial heterogeneity of soil properties and its mapping with apparent electrical conductivity. *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde* **2008,** *171*, (2), 146-154.

55. Sudduth, K. A.; Kitchen, N. R.; Wiebold, W. J.; Batchelor, W. D.; Bollero, G. A.; Bullock, D. G.; Clay, D. E.; Palm, H. L.; Pierce, F. J.; Schuler, R. T.; Thelen, K. D., Relating apparent electrical conductivity to soil properties across the north-central USA. *Comput. Electron. Agric.* **2005,** *46*, (1–3), 263-283.

56. Wu, F.; Mu, Y.; Chang, H.; Zhao, X.; Giesy, J. P.; Wu, K. B., Predicting Water Quality Criteria for Protecting Aquatic Life from Physicochemical Properties of Metals or Metalloids. *Environ. Sci. Technol.* **2012,** *47*, (1), 446-453.

57. Posthuma, L.; De Zwart, D., Predicted effects of toxicant mixtures are confirmed by changes in fish species assemblages in Ohio, USA, Rivers. *Environ. Toxicol. Chem.* **2006,** *25*, (4), 1094-1105.

58. Posthuma, L.; de Zwart, D., Predicted mixture toxic pressure relates to observed fraction of benthic macrofauna species impacted by contaminant mixtures. *Environ. Toxicol. Chem.* **2012,** *31*, (9), 2175-2188.

59. Hurd, L. E.; Mellinger, M. V.; Wolf, L. L.; McNaughton, S. J., Stability and diversity at three trophic levels in terrestrial successional ecosystems. *Science* **1971,** *173*, (4002), 1134-1136.

60. Skeaff, J.; Delbeke, K.; Van Assche, F.; Conard, B., A critical surface area concept for acute hazard classification of relatively insoluble metal-containing powders in aquatic environments. *Environ. Toxicol. Chem.* **2000,** *19*, (6), 1681-1691.

61. Ispas, C.; Andreescu, D.; Patel, A.; Goia, D. V.; Andreescu, S.; Wallace, K. N., Toxicity and developmental defects of different sizes and shape nickel nanoparticles in Zebrafish. *Environ. Sci. Technol.* **2009,** *43*, (16), 6349-6356.

62. Tourinho, P. S.; van Gestel, C. A. M.; Lofts, S.; Svendsen, C.; Soares, A. M. V. M.; Loureiro, S., Metal-based nanoparticles in soil: Fate, behavior, and effects on soil invertebrates. *Environ. Toxicol. Chem.* **2012,** *31*, (8), 1679-1692.

63. Ali, N. A.; Bernal, M. P.; Ater, M., Tolerance and bioaccumulation of copper in Phragmites australis and Zea mays. *Plant Soil* **2002,** *239*, (1), 103-111.